

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 April 2003 (10.04.2003)

PCT

(10) International Publication Number
WO 03/028977 A1

(51) International Patent Classification⁷: **B29C 47/06**

(21) International Application Number: PCT/US02/31553

(22) International Filing Date: 3 October 2002 (03.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/326,457 3 October 2001 (03.10.2001) US

(71) Applicant and

(72) Inventor: HEKAL, Ihab, M. [US/US]; 230 Round Hill Road, Greenwich, CT 06831 (US).

(74) Agent: HOLT, William, H.; Law Offices of William H. Holt, Unit 2 - First Floor, 1423 Powhatan Street, Alexandria, VA 22314 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/028977 A1

(54) Title: A FILM, AND METHOD OF FORMING, FOR IN-SITU CONTROLLED PRODUCTION OF SO₂ GASES

(57) Abstract: A method for producing a film for emitting sulfur dioxide, and the film produced thereby, wherein the method comprises the steps of simultaneously extruding a plurality of layers of polymers, wherein a first one of the layers contains a mixture comprised of sodium metabisulfite, sodium bisulfite or sodium sulfite in a powder dispersion, a second one of the layers containing a dispersion of an acid or an acid anhydride.

A FILM, AND METHOD OF FORMING, FOR IN-SITU CONTROLLED
PRODUCTION OF SO₂ GASES

One approach of the technology is embodied in co-extruded material comprising multiple layers, or sheets in the form of films, pads, and the like. A first layer may be comprised of, for example, polyethylene or polypropylene, or similar plastic. A second layer, sheet or film is comprised of reactive material which, in the presence of moisture can emit a Food and Drug Administration (FDA) approval, non-oxidizing gas that has mold inhibiting and deoxidizing properties. The gas is particularly not chlorine or chlorine dioxide because those gases are oxidizing gases.

The material is useful for packaging foods such a fruits, vegetables, dairy and bakery products, and other products susceptible to mold, to increase such products traveling and shelf life.

The concentration of the gas emitted from this material into a food package need only be approximately 1-100 parts per million, but may be more. If the package is substantially closed, the accumulated gas will readily dissipate when the package is opened. If desired, the package may contain perforations so that it will "breathe"; in such a case, the gas emission rate can be simply increased to compensate for the leakage of gas through the perforations.

The material can be used, for example, to wrap pallets of fruit, or may be converted into bags to hold grapes and the like, or may be used as a cover or wrap for baskets of fruit or berries, etc. In another form of the invention, the material can be extruded in thicker layers, sheets or films and formed into small pad-like members to be inserted into the conventional absorbent pads that are commonly used on the bottom of plastic

baskets, or "clam shells," or wrapped meat products and the like, all without changing existing packaging techniques.

One test that has been performed included a sample of ten baskets of raspberries purchased at an East Coast supermarket. A co-extruded pad of material was placed in the package which was then wrapped with the usual standard plastic film. The test showed a marked improvement in inhibiting mold progression within the packages in that there was no obvious mold and the shelf life increased from three (3) days to ten (10) days.

10

Summary of the Invention

15

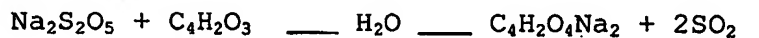
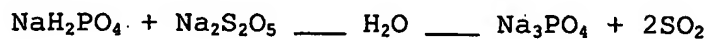
The invention is primarily comprised of a method for producing a film for emitting sulfur dioxide, and the film produced thereby, wherein the method comprises the steps of simultaneously extruding a plurality of layers of polymers, wherein a first one of the layers contains a mixture comprised of sodium metabisulfite, sodium bisulfite or sodium sulfite in a powder dispersion, a second one of the layers containing a dispersion of an acid or an acid anhydride.

20

Further, one form of the invention is based upon the slow emission of sulfur dioxide (SO₂) which can be created by reacting sodium metabisulfite (Na₂S₂O₅) or a derivative, e.g., with an acid or acid anhydride which, in the presence of water will produce SO₂. Typical reactions would be in the form of

25

and



These reactions are, per se, well-known, as is the use of sulfites and bisulfites to inhibit the growth of mold. However, it is a novel feature of the present invention to produce sulfur

dioxide in minute quantities for extended lengths of time for inhibiting the growth of mold.

5 In a particular novel form of the invention, one can encapsulate $\text{Na}_2\text{S}_2\text{O}_5$ with an acid or acid anhydride in a low melting temperature polymer such as low density polyethylene, or polyolefin, or vinyl acetate, to produce SO_2 in the presence of moisture.

10 In a variation on the invention, concentrated mixtures of the constituents can be marketed in the form of additives which can be added to polymers during formation of the sheets, layers, films and/or pads and during injection molding so that the packages are active in inhibiting the growth of mold.

15 In a further embodiment of the invention, the layers, sheets, films or pads can be co-extruded in two or more layers to control the emission of SO_2 and to keep the SO_2 confined to the inside of the container and the outside layer, or film, would function as a barrier to preclude escape of the gas. A thin third layer on the inside of the container or package would control the gas emission and control the ingress of moisture to
20 the sodium metabisulfite and the acid mixture.

As mentioned above, a few parts per million of SO_2 is sufficient to keep mold from spreading. In a controlled atmosphere, the addition of such a small amount of SO_2 to that atmosphere will inhibit the growth of microorganisms, including
25 mold.

Compounds for producing SO_2 gas can be mixed with polymers including polyolefins, polystyrene, polyamides, polyamines, polyurethane, vinyls (PVC, PVA, PVOH, PEVOH, PVP, etc.), polylactic acid, polyglycols, polyethylene oxide, cellulose and
30 derivatives (viscose (cellulose acetate, propionate, butyrate), hydroxyethyl cellulose, hydroxypropyl methyl cellulose, etc.).

For long distance shipping of fairly large boxes, such as for the shipment of tropical fruits, it is contemplated that small pouches formed of Tyvec and containing sodium metabisulfite and citric acid would be ideal because the boxes and pouches would be exposed to relatively high temperature and high humidity which, as is well-known, would promote growth of mold in the absence of the pouches formed in accord with the present invention. The amount of gas and the rate of production can be readily estimated and the pouch would be designed accordingly.

When the invention is to be used with smaller packages for the purpose of extending shelf life, for example, with "clam shells" used for berries and the like, a small piece of the inventive sheet material, on the order of 10-50 mils and, perhaps 1" x 1", or 2" x 2", can be placed inside the soft pad usually positioned at the bottom of the container for cushioning the product.

A variation of the foregoing would be forming the clam shell box from co-extruded plastics wherein the inside layer emits SO_2 gas and the outer layer provides a barrier against escaping gas.

A still further variation would be to wrap the small box of fruit with co-extruded film, the inside layer of which would emit the SO_2 gas.

I Claim:

1. A method of producing a film for emitting sulfur dioxide, said method comprising the steps of simultaneously co-extruding a plurality of layers of polymers, a first one of said layers
5 containing a mixture comprised of sodium metabisulfite, sodium bisulfite or sodium sulfite in a powder dispersion, a second one of said layers containing a dispersion of an acid or an acid anhydride.

2. A method as defined in claim 1 wherein said film further
10 includes a third polymer layer which is compatible with said first and second layers of polymers, and said method further includes the step of extruding said mixture at a temperature below 210 degrees F., preferably between 170 degrees F. and 190 degrees F.

15 3. A method as defined in claim 1 wherein said acid is citric acid, sodium di-hydrogenphosphate, and said anhydride is maleic anhydride or acidic anhydride.

4. A method as defined in claim 1 wherein said polymers for
20 forming said layers are selected from the group consisting of ultra low density polyethylene, atactic polypropylene, EVA, PVA, PMA, PEMA, polyglycoles, polyesters, wax, rosins, plasticized rubbers and PVC, and extrudable at temperatures below 210 degrees F.

5. A method as defined in claim 2 wherein said first,
25 second and third layers of polymers are co-extruded for forming said film having three layers, said mixture being disposed in a central one of said three layers between a pair of outer layers.

6. A method as defined in claim 5 wherein one of said pair of outer layers comprises a layer of greater thickness than the

other of said pair of outer layers.

7. A method as defined in claim 6 wherein said layer of greater thickness comprises a barrier layer for blocking passage of said sulfur dioxide.

5 8. A co-extruded film having a plurality of layers, a first of said layers containing a mixture comprised of sodium metabisulfite, sodium bisulfite or sodium sulfite in a powder dispersion, and a second one of said layers containing a dispersion of an acid or an acid anhydride.

10 9. A co-extruded film as defined in claim 8 further including a third polymer layer which is compatible with said first and second layers of polymers, and said film includes a third polymer layer which is compatible with said first and second layers of polymers, and said film having been formed at a
15 temperature within the range of 170 degrees to 190 degrees F.

10. A co-extruded film as defined in claim 8 wherein said acid is citric acid, sodium di-hydrogenphosphate, and said anhydride is maleic anhydride or acidic anhydride.

20 11. A co-extruded film as defined in claim and wherein said first, second and third layers of polymers are co-extruded for forming said film having three layers, said mixture being disposed in a central one of said three layers between a pair of outer layers.

25 12. A co-extruded film as defined in claim 11 wherein one of said pair of outer layers comprises a layer of greater thickness than the other of said pair of outer layers.

13. A co-extruded film as defined in claim 12 wherein said layer of greater thickness comprises a barrier layer for blocking

passage of said sulfur dioxide.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/31553

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : B29C 47/06 US CL : 264/171.1, 173.12, 173.16, 173.19, 211,349 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 264/171.1, 173.12, 173.16, 173.19, 211,349 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Please See Continuation Sheet		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94/10233 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION), 11 May 1994 (11.05.94), see entire document.	1
Y		2-13
Y	US 3,928,577 A (KOCHUROVA et al) 23 December 1975 (23.12.1975), see entire document.	1-13
A	US 4,490,330 A (HOWES et al) 25 December 1984 (25.12.1984), see entire document.	1-13
A	US 4,128,397 A (LYNCH) 05 December 1978 (05.12.1978), see entire document.	1-13
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier application or patent published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 12 December 2002 (12.12.2002)		Date of mailing of the international search report 08 JAN 2003
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230		Authorized officer Mark Eashoo Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

PCT/US02/31553

Continuation of B. FIELDS SEARCHED Item 3:

EAST

search terms: film liberate, emit, release, sulfur dioxide